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GRATING FORMATION IN DIAZO SALT (SENSITIZED) GELATIN.(U)
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# GRATING FORMATION IN DIAZO SALT (SENSITIZED) GELATIN

BY

J. W. GLADDEN

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Diazo (sensitized) gelatins are photosensitive recording materials that unlike dichromated gelatin have a long shelf life. Because of their stability, the diazo emulsions have replaced the dichromated colloids used in the photolithographic field and enabled commercialization of presensitized printing plates. We have produced plane wave gratings with peak efficiencies near 67% at an exposure of 625 mJ/cm² and a recording wavelength of 488.0 nm in one diazo recording material. Called diazo salt (sensitized) gelatin, the photosensitive material produces gratings in gelatin by a complex process that we found not to be a function

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of exposure. The methods used are described.

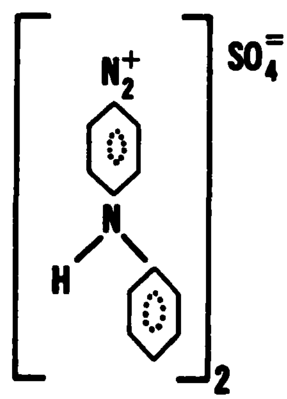
# GRATING FORMATION IN DIAZO SALT (SENSITIZED) GELATIN

J. W. GLADDEN, U.S. Army Engineer Topographic Laboratories, Center for Coherent Optics, Fort Belvoir, Virginia 22060.

Diazo (sensitized) gelatins are photosensitive recording materials that unlike dichromated gelatin have a long shelf life. Because of their stability, the diazo emulsions have replaced the dichromated colloids used in the photolithographic field and enabled commercialization of presensitized printing plates. We have produced plane wave gratings with peak efficiencies near 67% at an exposure of 625 mJ/cm$^2$ and a recording wavelength of 488.0 nm in one diazo recording material. Called diazo salt (sensitized) gelatin, the photosensitive material produces gratings in gelatin by a complex process that we found not to be a function of exposure. The methods used are described.

Not all potential holographic recording materials that form highly efficient gratings do so in a controlled manner that is dependent upon exposure. Such is the nature of the diazo (sensitized) gelatins. But this property is not disclosed by an examination of the material's characteristic exposure curve alone. It only became apparent following examination of the material by methods that are disclosed in this paper. We will begin by introducing the diazo gelatins that are described in the patent literature [1,2] and then briefly describe the methods used to evaluate their suitability for holographic recording.

The diazo salts are a class of aromatic organic compounds having the general formula $ArN_2^+ X^-$. Here $X^-$ is one of a large number of anions such as $Cl^-$, $HSO_4^-$, $BF_4^-$, etc. The aromatic ring is one selected from benzene, naphthalene and their derivatives. We selected para-diazodiphenylamine sulfate which has the following chemical formula:



This compound was obtained from Chemicals Procurement Laboratories, Inc.[3] P-Diazodiphenylamine sulfate is VIS light sensitive, and its photolysis product appears to cross-link or tan gelatin directly.

The essential steps in preparing and processing diazo salt gelatin plates are similar to those used in the preparation and processing of dichromated gelatin layers. These steps in-

volve fixing and drying a Kodak 649F plate, sensitizing the plate in a 1% solution of p-diazodiphenylamine sulfate, drying, exposing, washing in room temperature running water for 10 minutes, dehydrating in a 50% solution of isopropanol followed by 100% isopropanol bath for 3 minutes each, air drying for 10 minutes, and finally oven drying at 82°C for 2 hours. The 649F plates were fixed in Kodak F-24 non-hardening fix. The exposures were carried out using a plane wave pattern of 1580 c/mm at 488.0 nm. The plane wave gratings are found to be diffracting following exposure. The efficiencies increase with completion of the processing procedure.

The characteristic exposure curve for the plane wave gratings prepared using the diazo salt gelatin process is shown in Figure 1. An argon ion laser with total intensity near 8.1 mW/cm$^2$ at 488.0 nm was used to expose the 39 gratings on two separate plates. The interbeam ratio of light intensities (K-value) was 1.05. A peak efficiency of 67.5% is observed near an exposure of 625 mJ/cm$^2$. The angular band width was measured for different exposures and found to be 3 degrees full width---half maximum.

Figure 2 shows two characteristic exposure curves whose efficiencies were determined at two different times during the preparation of the gratings. For the curve recorded at 632.8 nm, the first order intensity was measured at that wavelength immediately following exposure to the interference pattern at 488.0 nm. The efficiencies at 488.0

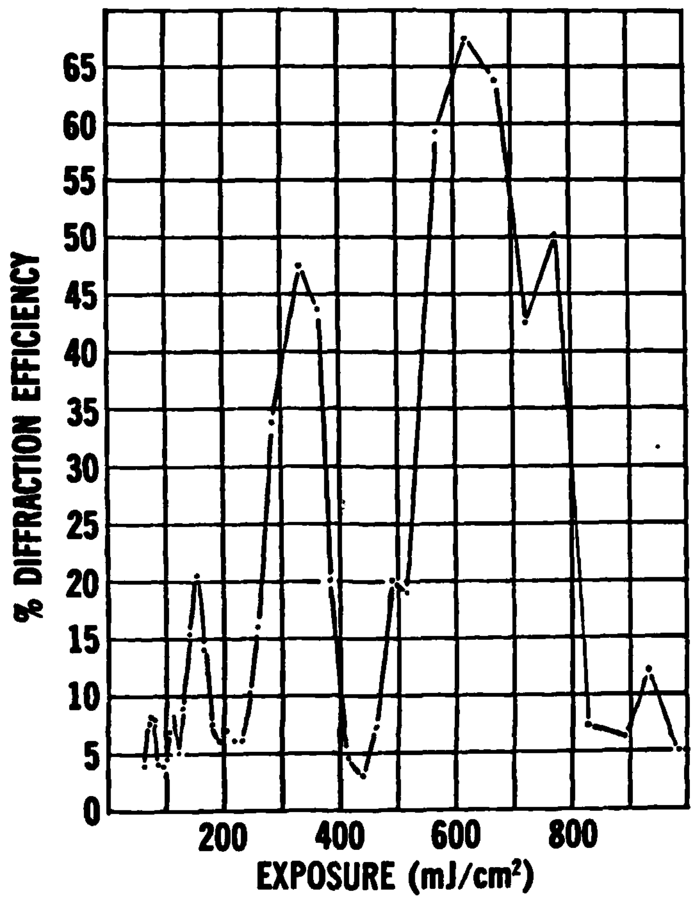



Figure 1. Characteristic Exposure Curve For Diazo Salt Gelatin

nm were determined following processing the 15 plane wave gratings. It is interesting to note that between the exposures 340 and 630 $mJ/cm^2$, the peak and troughs on the 632.8 nm curve correspond with troughs and peaks respectively on the 488.0 curve.

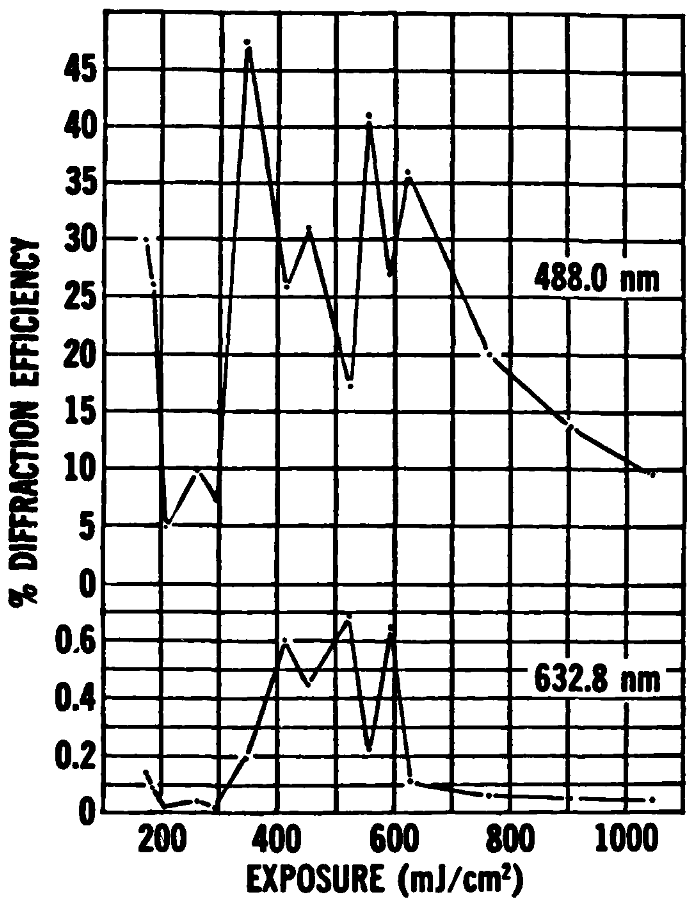



Figure 2. Comparison of efficiencies following exposure with that of the grating following processing in diazo salt gelatin.

Figure 3 describes the efficiency of the grating being formed during exposure. Absent in the curve is evidence of any peaks and troughs being formed during exposure. This result when considered in view of Figure 2 suggests that the mechanism for grating formation, and the resulting diffraction efficiency is not a predictable function of exposure. This will be further discussed shortly. But to test

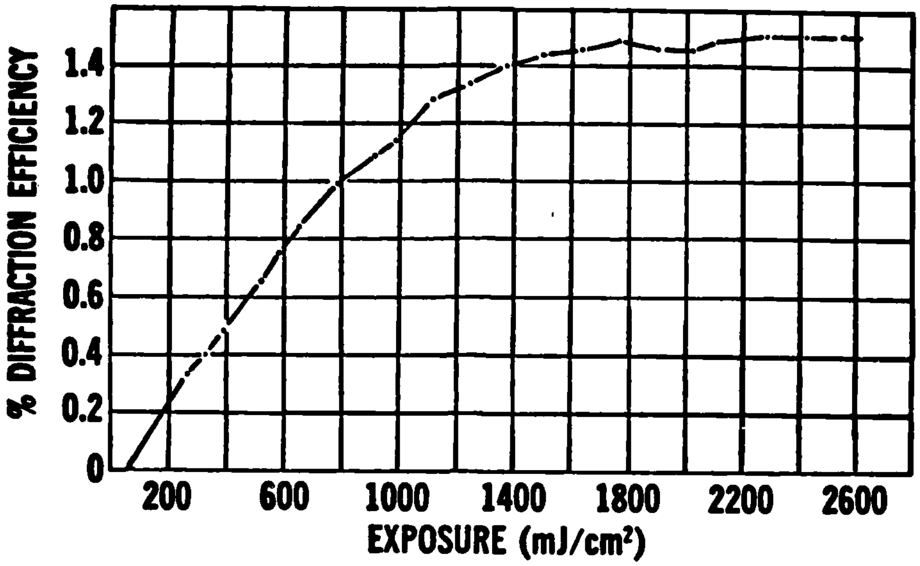



Figure 3. Efficiency of grating at 632.8 nm during exposure at 488.0 nm.

this, four series of seven to ten plane wave gratings each were prepared using seven to ten identical exposures. Up to twenty plane wave gratings were recorded on each 100 by 125 mm plate in rows of five each. Figure 4 describes these statistics. Please note that as the experiment was designed, both good and bad holograms appeared in the interior of the plate as well as near the edges. The results displayed in the figure show that the efficiency appears dependent upon the position of the grating on the plate. There would be a row of five good gratings (i.e. positions 1-5) followed by a row of relative poor gratings (i.e. positions 6-10). No obvious dependence of efficiency on exposure is observed.

The formaldehyde condensate of p-diazodiphenylamine sulfate was also prepared using a procedure described in the patent literature.[4]

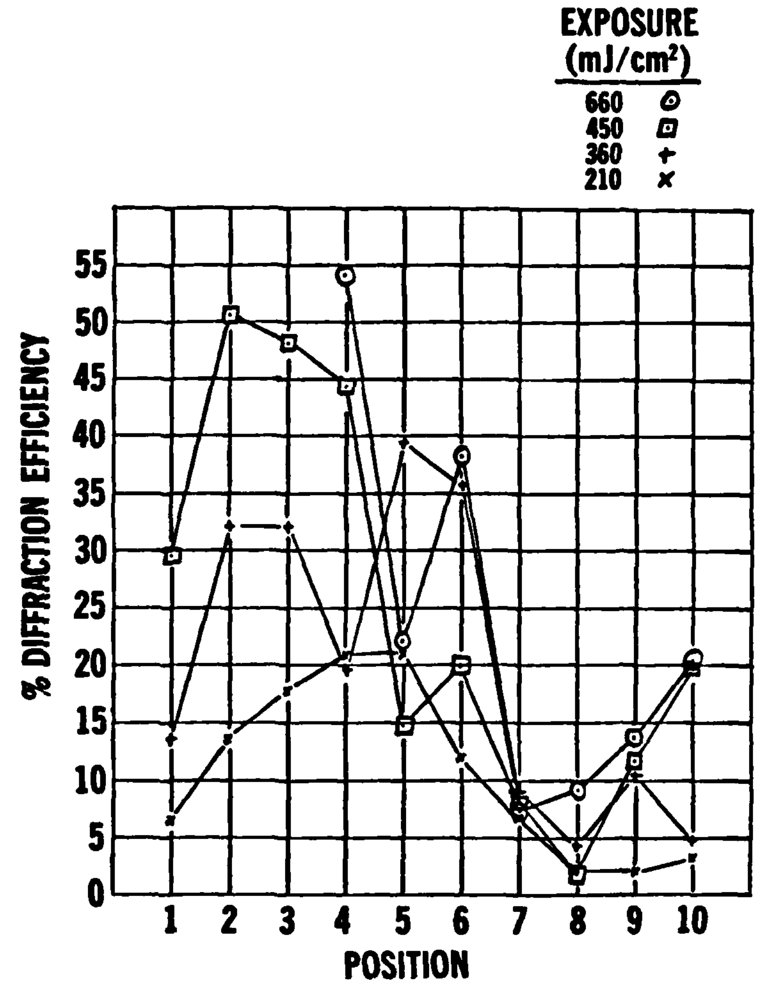



Figure 4. Statistics of Identical exposures in diazo salt gelatin.

The diazo resin formed was used to prepare 1% solutions for the sensitization of gelatin plates. The preparation, exposure, and processing procedures were the same used for the diazo salt. Successful plane wave gratings were prepared with the diazo resin (sensitized) gelatin plates. Efficiencies on the order of 15% at

exposures between 525 and 925 $mJ/cm^2$ were obtained at a recording wavelength of 488.0 nm. The characteristic exposure curve was also oscillatory in nature. A study of the statistics of series of ten identical exposures given diazo resin gelatin plates indicated no observable dependency of efficiency with either exposure or position of the grating on the plate. Formation of the grating and its resulting diffraction efficiency were completely uncontrolled in this case.

One needs to understand that the recording procedure adopted was designed to produce a stable recording environment for the time of the exposures which lasted nearly two minutes at most. The recording optical arrangements that included an interferometer and procedure will be found described elsewhere in this issue in an article by Graver, Gladden, and Eastes. The fringe stability during recording is further attested to by the data shown in Figure 3. It is doubtful that the plateau would be observed if there were any instability in the recording arrangements.

The diffraction efficiency was measured as a quotient of the power diffrated into the first order beam and the power in the incident beam of light on the surface of the grating. As such, the measurement does not exclude losses due to absorption, scattering, or reflection. Perhaps a significant loss is in the absorption afforded by a photolyzed product of the diazo compound.

An examination of Figure 3 does depict an efficiency that increases to a maximum with exposure and does appear to indicate that the diffraction efficiency of the diazo salt (sensitized) gelatin is a function of exposure. This is true for the singular exposure event, but the function is not found to be constant when examined in view of a number of exposure events. The effect is not unlike that observed by Materazzi[5] in a study in which commercial, diazo resin plates were developed using an ink receptive lacquer. The lacquer weight deposited on the presentized printing plate was found to produce an oscillatory function with exposure that is of a similar nature to that shown in Figures 1 and 2. Materazzi concluded that photolysis of the diazo resin emulsion does not proceed in a uniform manner. He believed that different species of polymers are produced at different exposures and that each polymer specie had a different affinity for the developer lacquer. In the cases of the diazo salt and diazo resin gelatins, the chemical processes appear to be even more varied than this. It is a spatial variation in the chemistry within the gelatin emulsion that appears to produce the variation in results as depicted in Figure 4.

The chemical processes occurring in diazo salt gelatin are numerous[6] and appear to account for the complex process by which grating formation occurs. First photolysis of the diazo salt releases nitrogen gas in the gelatin matrix. The nitrogen may be trapped within the gelatin there to expand upon processing forming a vesicular image.

Or the nitrogen may slowly diffuse out of the gelatin producing very little effect in the grating formation. In a polar environment such as promoted by the presence of water, photolysis produces a phenol which in the case of p-diazodiphenylamine sulfate results in a compound that may cross-link gelatin directly. In a non-polar environment, photolysis of the diazo salt would produce free radicals that if formed in gelatin would also promote its cross-linking. It may be possible for the diazo salt to photolyze forming phenols initially in gelatin and then proceed to cross-link gelatin by a free radical process. Thus, the real mechanism for grating formation in diazo salt gelatin appears dependent upon the chemical nature of the gelatin matrix, and that changes as photolysis proceeds. The results may be accounted for by non-uniform sensitization of the gelatin plates but this appears improbable in that visual checks disclosed a fine uniform coloration of the emulsion. It appears more probable that the results are due to some process such as either a non-uniform distribution of moisture in the emulsion or to some artifact that may promote differential entrapment of the evolved nitrogen. Then too, this may be the result of the manufacturing procedure for the gelatin emulsion. This must be considered because of the trend in data depicted by Figure 4. Also we were able to generally reproduce the data exhibit in Figure 1. The significant difference in the appearance of the data between Figures 1 and 2 is attributed to the change in position for the

individual exposures on the two different plates.

In regards to the useable shelf life of the diazo resin (sensitized) gelatin, we exposed and processed sensitized plates that were stored in the ambient for three weeks with no observable deterioration in the peak efficiency obtained. We would expect a similar result for the diazo salt (sensitized) gelatin plates but they were not studied for shelf life.

There may be hope for the future improvement of diazo salt (sensitized) gelatin. There are procedures described in the patent literature that may be tried. These will be found described in a report available from the author[7] and include developing the exposed diazo gelatin plates in dichromated solutions and/or warm solutions or water.

In summary, we have shown that it is possible to prepare plane wave gratings in diazo salt (sensitized) and diazo resin (sensitized) gelatins. Although efficiencies in excess of 67% were observed in diazo salt gelatin, we did not observe any dependency of the formation of the gratings with exposure. An examination of the Figures 2 and 3 suggests that the formation of gratings during the exposure step is arbitrary and that the efficiencies of the gratings following processing are mostly inversely related to the same gratings following exposure. Considering these results and an analysis of the different chemical processes that can occur in the diazo gelatins

suggest that grating formation in the diazo gelatins is a complex process that we found not to be a function of exposure. This result is supported by the statistics of preparing gratings given ten identical exposures.

The author wishes to thank Dr. John W. Eastes of the Center for Coherent Optics for his discussions particularly of the Materazzi effect and his assistance in the laboratory work.

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Figure 1. Characteristic Exposure Curve For Diazo Salt Gelatin.

Figure 2. Comparison of efficiencies following exposure with that of the grating following processing in diazo salt gelatin.

Figure 3. Efficiency of grating at 632.8 nm during exposure at 488.C nm.

Figure 4. Statistics of identical exposures in diazo salt gelatin.